DETERMINATION OF BENZENE
IN HYDROCARBONS

BY

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Determination of Benzene and its Derivatives in Admixtures with Paraffin Hydrocarbons

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A THESIS

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Benzene was discovered in 1825 by Faraday, in the liquid obtained from compressed oil gas. In 1846 its isolation from coal tar, one of the important sources, was accomplished by H.W.Hofmann. Since that time , its use has become very extensive.

At one time this hydrocarbon was used principally as a source of supply for other aromatic bodies. This was especially true during the recent war, when the demand for high explosives greatly exceeded the supply. During this critical period all efforts were bent on obtaining benzene and its homologues for use in ammunitions. Every source of supply was utilized regardless of the cost of recovery. But this was an abnormal condition and consequently could not exist after

the emergency had passed. All the
processes which were very expensive
to operate have been or are being
abondoned. The sudden decline in the
demand, after a period of intensive
production, left a great excess supply
which could not be absorbed by the
chemical industries, whose demands
are normally supplied by recovery from
by-product coke-oven installations.
An attempt has been made to utilize
this excess as a motor, either when
in the pure state or when mixed in
varying amounts with gasoline.

Since this is the outlook, some
method for the determination of benzene
when mixed with other components of
an oil, especially the paraffin hydro-
carbons, must be developed. It must
be applicable for general laboratory

use, permitting rapid analysis and accurate results. It is in view of this demand that the present work has been undertaken.

Needless to say there has been previous work done on the quantitative determination of benzene in all sorts of mixtures. A survey of the literature will give a comprehensive view of the mass of material presented, and the difficulty of selecting a method which is suited to the work in hand. The bibliography given in this report includes the important material done on this subject up to the present time.

In the estimation of benzene, its physical and chemical properties form the basis of attach. This being the case most all its properties have at one

time or another been used in an attempt
to develope a satisfactory method of
analysis. Some of the properties which
have been used are: boiling point,
freezing point, specific gravity,
solubility, refractive index, surface
tension, viscosity, "molecular weight"
or the effect on the boiling point or
freezing point when in solution, and
definite chemical reactions such as
nitration, sulfonation, etc.

A survey of these methods shows that
few of them are practically applicable
to the problem at hand. A short and
satisfactory summary of them is given
by a government publication[1] which is
quoted in part:
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1). "Manufacture of Gasoline and Benzene-
Toluene from Petroleum and Other Hydro-
carbons." Bulletin 114. Petroleum
Technology 29.

"Surface tension is readily influenced by the presence of small quantities of impurities and, in the absence of definite knowledge concerning its nature, is of little importance. "Molecular weights" have been shown to be unreliable even when determined for mixtures that are chemically more homogeneous than those obtained in the present work.

Separation through differences in boiling point needs little discussion. That benzene, toluene, and xylene can be separated by distillation is indicated by the differences in their boiling points, which are as follows: benzene, 80.4°C.; toluene, 110.3°C.; xylene, 138°C.

However, although the three aromatic hydrocarbons may be separated from each other by retification they cannot be isolated from the aliphatic hydrocarbons that are present in the cracked oil and have boiling points approximately the same as those of benzene, toluene, and xylene. In the determination of the aromatic compounds wide differences between the specific gravities of the aromatic hydrocarbons and those of the other constitutents of approximately like volatility were of great aid.

The refractive index is closely related to specific gravity, and on account of that relation did not demand special consideration. Viscosity is not an additive

property. In actual fact, information was needed regarding only the first four of the properties listed.

The use of dimethlysulfate as a solvent has been investigated by Valenta, Perkin and Harrison, Chapin, Reeve and Lewis, Sommer, Church and Weiss, and by Rittman, Twomey, and Egloff. The only logical conclusion to be had from a review of these researches is that this method is not be to recommended.

Owing to the relatively high freezing point of benzene, various investigators have recommended that the benzene content of an oil be quantitatively estimated by a freezing method.

Some experiments, therefore, were conducted with known mixtures of benzene and unrefined gasoline with a specific gravity of 0.728. ------ These results indicate that benzene crystals tend to include so much mother liquor that the freezing method for the determining of benzene is unreliable. It appears also that in the presence of an excess of nonaromatic constitutents the benzene crystals may either be prevented from separating out or may be dissolved as soon as formed. In any event the freezing method seems to have little to recommend it.

Prevoius considerations indicate that the most promising physical property on which to base analytical methods was specific gravity. By making use of the differences in gravities of aromatic and non-aromatic hydrocarbons at the same temperatures it was possible to estimate with some accuracy the content of aromatic hydrocarbons. This method required a knowledge of the average specific gravity of nonaromatic constitutents, and values were assumed that had been indicated as the results of much experience. In order to check these the aromatic content of various distillates was determined by the standard chemical method of nitration. A close agreement was noted among results obtained by the two nethods --- the tedious one of nitration and the simple one of specific gravity."

According to this information supplied by the Department of Interior, the two methods worth considering are nitration and the determination of the specific gravity.

The method of nitration, which is conceded to be accurate but slow is

described by Lunge[1] as follows:

"Determining available benzene
in a mixture. G.Lungy ("Coal Tar
and Ammonia", 3rd. English Ed.,
p.626). recommends the nitration
test, which depends on the pro-
duction of nitrobenzene. He
describes it as follows: 100cc
of the sample are placed in a
500cc flask provided with a cork
carrying two tubes. A mixture of
150 gm. of HNO_3 (sp.g. 1.14), and
180 to 200 gm. of H_2SO_4 (sp. g.
1.84) is prepared and allowed to
cool. Portions of this mixture
are placed in the stoppered tube
and allowed to flow drop by drop
into the benzene, shaking this up
almost instantly. If the temperature
rises, the flask must be cooled by
immersion in water. When addition
of acid ceases to produce rise in
temperature the flask should be
heated gently for an hour or two,
during which time it will be an
advantage to connect the second
tube with a reflux condenser.
Allow the mixture to settle and
separate the layer by a separatory
funnel. Most ofthe crude nitro-
benzene is in the upper layer. The
lower (acid) layer should be
diluted with several times its
bulk of water and allowed to stand
for a few hours. Any oily liquid
separating should be added to the
nitrobenzene. Wash the latter with

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1)."Allan's Commercial Organic Analysis.

water several times, then with a very
dilute solution of NaOH, and once again
with water. Care should be taken that
none of the product is lost in these
washings. The washed nitrobenzene is
then allowed to settle, carefully
separated, redistilled in a fraction-
ating flask until the temperature of
150° is reached and the distillate
once more nitrated, using large excess
of the acid mixture. Any material
remaining undissolved may be regarded
as nonaromatic hydrocarbons. 157.6 parts
of nitrobenzene correspond to 100 parts
of pure benzene."

In preference to this method the Department
of Interior recommends that of specific
gravities referring the values obtained to a
chart of specific gravity and percentage
composition.

In order to approach the accuracy of the
nitration method and the speed of the specific
gravity determination, W.Mendius[1] recommends
that we determine benzene and its derivatives
by bromination to dibrombenzene. His method

1). The Determination of Benzene in Petroleum
Distillate.

is as follows:

"The specific gravity of the oil to
be tested is determined and 0.1cc or
about 0.1gm of it is introduced into a
clean and dry test bottle, which already
contains the 0.02gm of pure 200 mesh iron.
The author recommends the use of a bottle
as shown in Fig.11. Just enough carbon
bisulfide is then added to dissolve the
oil, say about 5cc. Enough N/1 bromine
solution is added to furnish the bromine
for the iron (0.0579gm. Br.) and the
bromine to form dibrombenzene (0.360 gm.
Br.) assuming the oil to be pure benzene.
This is to furnish sufficient excess to
brominate. The bottle is immediately
stoppered, water sealed and let stand
for one hour at 35°C. A blank test should
be made with every series of tests to
standardize the bromine solution. At the
end of one hour the flask is cooled,
the stopper removed and washed, and an
excess of potassium iodide solution
added. The mixture is throughly
agitated. The free iodine which is
liberated by the equivalent amount of
bromine not absorbed is titrated with
1/5th normal solution of sodium thio-
sulfate using starch to aid in the
detection of the end point, which is the
final disappearance of the blue color.
Much agitation is necessary. Knowing
the standard and relation of the two
solutions the amount of bromine absorbed
is calculated. This is the difference
between the amount of bromine solution
equivalent of the thiosulfate solution,
times the standard of the bromine
solution. The amount of the bromine
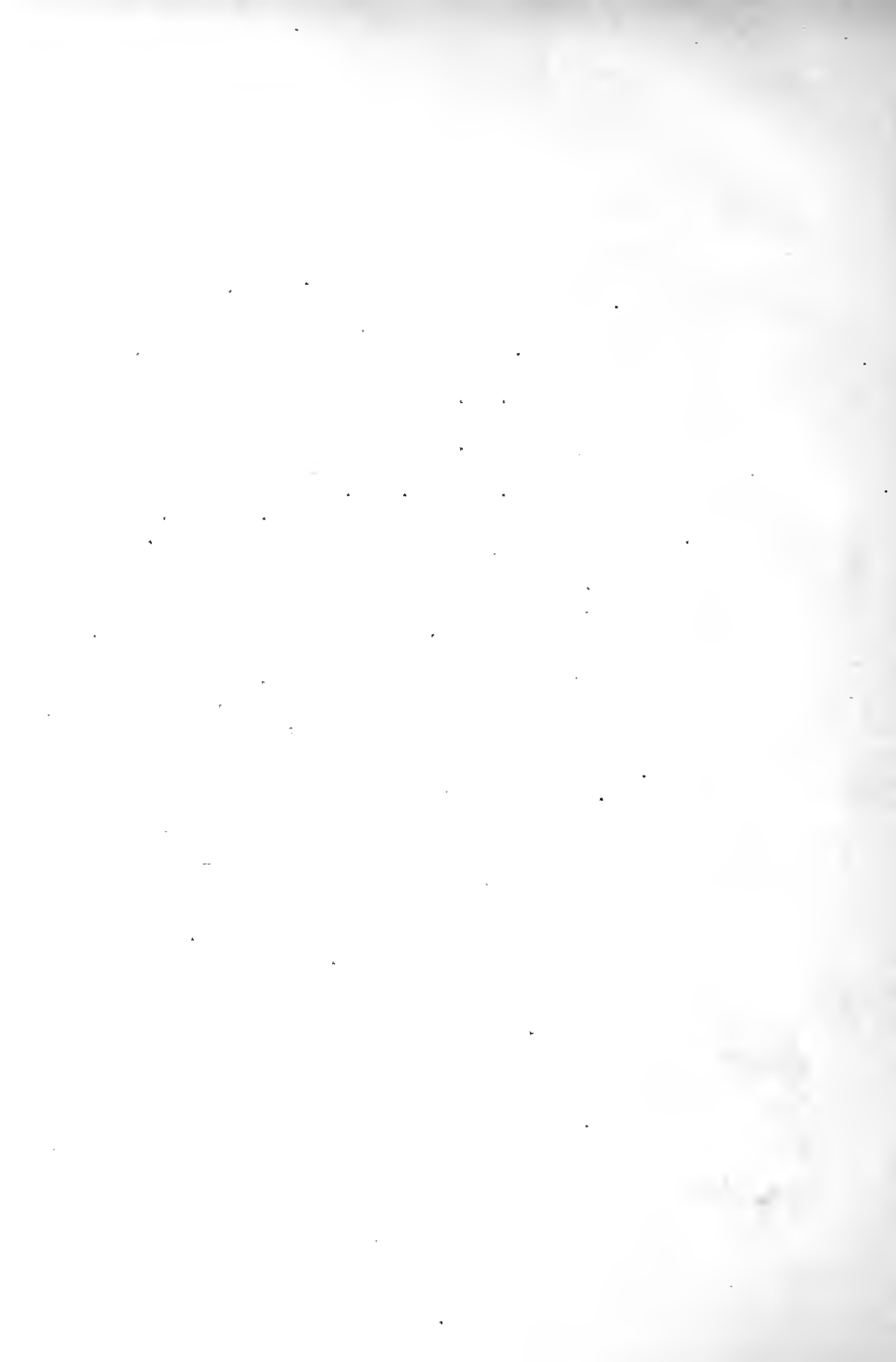
> reacting with the iron is subtracted
> from this amount. The resulting figure
> is the amount absorbed by the benzene
> and the olefines. From this is subtracted
> the amount of bromine absorbed by the
> olefines ---. The benzene is divided by
> 4.094 which gives the weight of benzene
> in the oil. With this data the percent-
> age, by weight, of benzene in the oil
> can easily be calculated."

This work is based on the above method:
the scope of the undertaking being to duplicate
the results if possible, and then to apply the
method in a general way by using known
mixtures.

Benzene of the highest degree of purity
was prepared by treating commercial benzol
with concentrated H_2SO_4 and dilute caustic:
then fractionally distilling; preserving
only the benzene fraction. Purification was
further continued by distillation until the
entire fraction boiled within two degrees of
80^oC. Finnaly the sample was subjected to
fractional crystallization until it froze
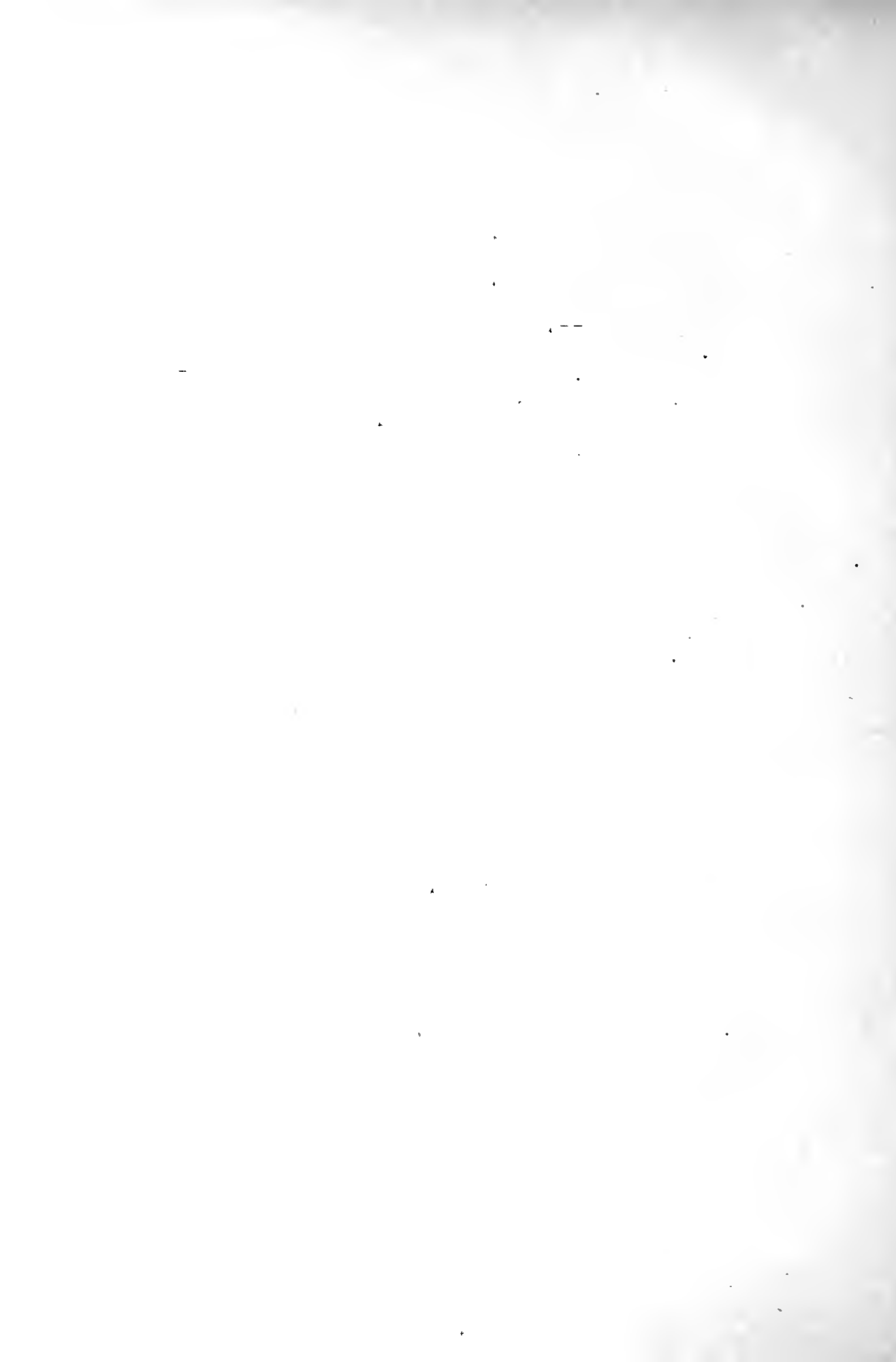
within $0.1^{o}C$ of $5.48^{o}C$.

The first difficulty encountered in the method was that of getting an accurate sample of benzene either by volume or by weight. Several methods were tried. The first was that of using a burrette. This was found to be too inaccurate and permitted the vaporization of the sample. Weighing in Victor-Meyer bottles was tried. This gave an accurate weight, but the size of the mouth of the bottle did not permit sufficient contact to yield good results. Especially prepared bottles, made by blowing very thin walled glass tube into small bulbs, then drawing out the neck to form a very small opening, was tried. These were filled by immersion of the stem of the heated bulb into the benzene, which was sucked up as the bulb cooled. The difficulty in the use of these was due to the burning of the sample when an attempt was made to seal the stem.

Finally satisfactory volumes were obtained by the use of small standardized pipette graduated to 0.01cc. In this way the sample could be introduced into the carbon bisulfide, the solvent contained in the reagent bottle, and the volume of the sample be accurately known.

This search for a satisfactory way of obtaining a sample gave practice in developing the necessary technic. After the use of the pipette as giving the best results was decided upon, several runs were made to develop the proper proficiency in conducting the analysis. Results of this preliminary work are given in table 1. Through out the work the percentage of benzene entering the reaction is expressed on the basis of the formation of monobrombenzene.

The next step was the duplication of the results obtained in the previous work performed

on this subject. That this is possible is
shown in the results given in Table lll.
Table ll., obtained in the process of the
work done to assemble the data for Tablelll.,
indicates that in order to secure consistent
results the percent of bromine used for
bromination of the benzene must be over
207% of the amount necessary to form mono-
brombenzene. Tables lll. and lV. in addition
to proving that the product obtained is
dibrombenzene demonstrates that at least
242% bromine is necessary to give uniform
results. Also above the concentration of
approximately 250% and up to 625% bromine
the product is always the dibrom body.
Therefore in accordance with this data,
the concentration of bromine used will be
as near as possible to250%, but in every
case an excess rather than an insufficient
amount should be used.

The work done so far proves that on using samples of pure benzene and brominating, we get a uniform product of dibrombenzene, and that from data on the normality of the standard solutions we can quantitatively determine benzene by this method. This brings up the next step, that of trying the method out on known mixtures.

One thousand cc. of commercial gasoline were obtained and purified. The purification process consisted of repeated washing with concentrated H_2SO_4 until the acid remained clear on shaking with the gasoline. A 1% solution of caustic was added to neutralize the excesss acid. Water was used for the final washing. The gas was fractionally distilled, saving the portion which boiled between 80° and 140^OC. This distillate was dried over calcium chloride.
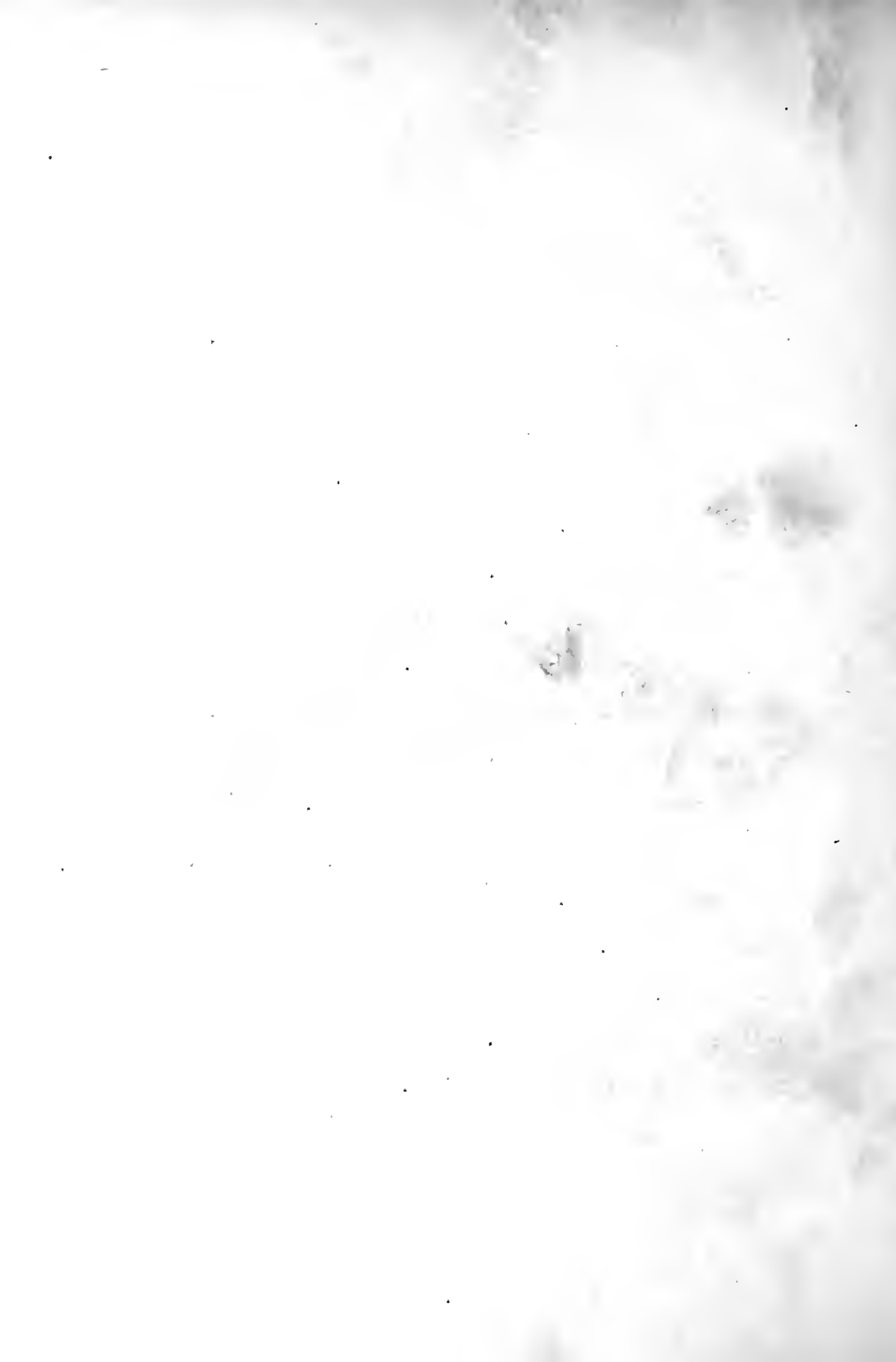
Since the product cannot be assumed to be free from unsaturated bodies, a test for them must be made. The method used was the standard one as given in Allan[1]:

"A 1/10th normal solution of bromine is made by dissolving 2cc of bromine in 750cc of recently distilled carbon disulfide and the solution, having been dried over calcium chloride crystals, is preserved in the dark.

From 0.3 to 1 gram of oil is weighed out in a perfectly dried stoppered flask or separator, the oil diluted if necessary with about 25cc of carbon disulfide. Then 25cc of the bromine solution is added, the flask stoppered, agitated and left in the dark for 15 minutes. If the liquid is not distinctly red after the agitation, a further quantity of bromine solution is added without delay. After 15 minutes an excess of an aqueous solution of KI is poured in, the mixture agitated. The bromine which was not absorbed by the oil having been replaced by an equivalent amount of free iodine, the flask is removed to a light place and the contents titrated with 1/10th normal solution of sodium thiosulfate. The titration is conducted in the usual manner, the final change being rendered more sharp by adding a few drops of starch solution when the

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1). Commercial Organic Analysis.

carbon bisulfide is nearly decolorized.

The bromine solution used requires
to be standardized ocassionally by
titrating 25cc. of the bromine solution
as above. The difference between the
volume of sodium thiosulfate solution
now required, and that used after treating
the oil, represents the volume corres-
ponding with the amount of bromine
absorbed."

The results of this analysis are shown
in Table V. The amount of unsaturated hydro-
carbons present is expressed as the number of
grams of bromine absorbed per cc. of the
gasoline. This amount is to be deducted from
the total amount of bromine used in the
future analyses involving gasoline, just
as in the case of the bromine absorbed by
the iron in the formation of ferrous
bromide.

In order to know how much benzene there
was per cc. of the gas, an analysis of it was
made following the same perscribed method as
given on page 10. The results proved to be
satisfactory and are set forth in Table Vl.

Mixtures of definite amounts of gas and benzene were made. See Table Vll. In the calculations the allowance for the bromine needed to form $FeCl_2$ and to brominate the unsaturated bodies was made. The total amount of benzene used in the tests is known since it is the sum of the amount of pure benzene plus the amount found to be present in the gasoline.

The results obtained show that the method described permits accurate work, but the accuracy of the results demands careful and accurate work on the part of the analyst.

Several tests were made with a view of making the method more rapid. The use of iron as a carrier necessitates the weighing of a definite amount of iron for each run. This involves time and trouble. In order to overcome this a carrier of another type was tried. A series of runs, with $FeCl_3$ as a

carrier, were made with the results shown in Table Vlll. These figures indicate that the absorption of bromine by benzene is very incomplete and varies within wide ranges, although the conditions are the same.

To add to the safety of the water seal around the stopper, the feasibility of putting a layer of water in the bottle was tried. The accuracy of the results was impaired, and the absorption greatly affected by the presence of the water. See Table lX.

In completing this report a mention of some of the precautions necessary to accuracy will not be out of place.

The data submitted in Table IX. shows that the presence of water is detrimental. Although the discrepancies are not as great when there is only a small amount of water, nevertheless the best results can only be expected when the container and the reagents

are perfectly dry. This detail must be care-
fully observed. The presence of moisture
during the analysis is indicated by the iron
adhering to the bottom of the bottle.

The standard solutions used should be of
low concentrations. This permits greater
accuracy due to the fact that an error of
several drops in running out the required
amounts is much less than wouldbe the case
if a more concentrated solution were used.
Especially is this true in the case of the
bromine solution for example were it was
observed that 10cc of the solution could be
drawn from the burette and another several
drops drawn out without the level of the
meniscus apparently changing. These few
drop may cause an appreciable error.

After the time for reaction has been
allowed, the bottles should be placed under
a cold water tap. This cooling of the bottle

and contents requires about 15 minutes. At
the end of this time the bottle may be
opened without loss of any of the sample
due to the pressure of the vaporized liquids
in the bottle.

Titrating with an excess of potassium
iodide (about 10%) gives a clear end point
and more satisfactory results than if less
is used. The outline of the method as given
on page 10 calls for vigorous shaking. This
was not found to be necessary and in fact
if the shaking is carried too far the values
are greatly impaired. That is to say, with
an excess of KI and moderate shaking the
best reults are obtained. When shaking is
carried too far the results obtained were too
low indicating that some of the bromine in
the dibrombenzene has been replaced by the
iodine. This fact is substantiated by the
reappearance of the blue color after standing.

In conclusion the method suggested has been found to be satisfactory. The product of bromination is always dibrombenzene. The accuracy of the results is equally good when using pure benzene mixed with other bodies as when using pure benzene. But as mentioned before, care and accuracy on the part of the analyst are a prime essential.

TABLES.

TABLE 1.

Bromination to DiBrombenzene.

Preliminary Tests.

Test No.	Bromine Used Wt.	%	Bromine Absorbed Wt.	%	Benzene Used	Determined	Error %
16	5.5564	617.3	2.8062	311.8	.4392	.6847	55.9
17	4.8144	550.7	2.4512	273.5	"	.5980	36.1
18	3.6341	403.7	1.8899	210.0	"	.4611	4.9
19	3.6077	400.8	1.8268	202.7	"	.4457	1.5
20	2.5361	281.8	1.9643	218.1	"	.4792	9.1
21	2.5361	281.8	1.7667	196.1	"	.4310	- 1.9

TABLE 11.

Determination of Percent

Bromine Necessary.

Test No.	Bromine Used Wt.	%	Bromine Absorbed Wt.	%	Benzene Used	Determined	Error %
22	1.8613	206.7	1.7029	189.2	.4392	.4155	- 5.40
23	"	"	1.6637	184.8	"	.4059	- 7.59
24	"	"	1.7020	189.1	"	.4152	- 5.40
26	"	"	1.6832	187.0	"	.4106	- 6.52
27	1.7927	199.2	1.6702	185.5	"	.4075	- 7.22

TABLE 111.

Determination of the Best Percent
of Benzene to Use.

Test No.	Bromine Used Wt.	%	Bromine Absorbed Wt.	%	Benzene Used	Determined	Error %
29	2.1812	242.4	1.8071	200.6	.4392	.4409	.39
30	"	"	1.8071	200.6	"	.4409	.39
31	"	"	1.8068	200.4	"	.4408	.38
32	"	"	1.8070	200.6	"	.4408	.38
34	2.7707	308.7	1.7939	199.6	"	.4377	- .35
35	3.6077	400.8	1.8076	200.3	"	.4410	.42
36	3.5985	399.8	1.8031	200.2	"	.4340	.16
37	5.6029	622.5	1.8030	200.2	"	.4339	.16

TABLE 1V.

Determination of the Best percent

of Benzene to Use.

Test No.	Bromine Used Wt.	%	Bromine Absorbed Wt.	%	Benzene Used	Determined	Error %
38	1.8619	207.0	1.6700	185.6	.4392	.4074	-7.22
39	2.4048	251.3	1.7973	199.7	.4392	.4385	.16
40	2.6625	295.7	1.8063	200.4	.4392	.4408	.38
41	3.6025	400.9	1.8072	200.8	.4392	.4409	.39
42	4.5329	503.6	1.7955	199.5	.4392	.4381	- .55
43	5.3345	592.7	1.8009	200.1	.4394	.4394	.00

TABLE V.

Determination of Unsaturated Bodies

in Gasoline.

Test No.	Gasoline Used	Bromine Used	Bromine Absorbed	Bromine = Unsaturated Bodies per cc. of gas
44	1.5cc.	.6625	.0285	0.0190
45	1.5	.6757	.0400	0.0266
46	2.0	.3975	.0180	0.0090
47	"	.3312	.0380	0.0190
49	"	"	.0380	0.0190
50	"	"	.0382	0.0191
51	"	"	.0380	0.0190
52	"	"	.0377	0.0188

TABLE Vl.

Determination of Benzene in Gasoline.

Test No.	Gasoline Used	Bromine Used	Absorbed	Benzene Determined Gms. per cc.
54	1cc.	1.2179	.3278	.0799
56	"	"	.3071	.0758
57	"	"	.3140	.0776
58	"	"	.3106	.0756
61	"	"	.3158	.0778
62	"	"	.3140	.0776
63	"	"	.3138	.0775
64	"	"	.3106	.0756
65	"	"	.3158	.0778
66	"	"	.3106	.0756

TABLE Vll.

Test Analyses of Known Mixtures.

Test No.	Bromine Used	Absorbed	Gas. Used	Benzene Used	Used	Determined	Error %
66	1.2179	.6677	1cc.	.1cc	.1654	.1630	-1.46
67	"	.6683	"	"	"	.1668	.80
68	"	.6686	"	"	"	.1673	1.10
69	"	.6679	"	"	"	.1660	.31
70	"	.6675	"	"	"	.1648	- .40
71	"	.6684	"	"	"	.1668	.80
73	1.9154	1.3934	1cc.	.3cc	.3411	.3410	.00
74	"	1.3852	"	"	"	.3380	- .90
75	"	1.4100	"	"	"	.3420	.2
77	"	1.3970	"	"	"	.3410	.00
78	"	1.3790	"	"	"	.3376	-1.00
79	"	1.3701	"	"	"	.3345	-2.00
80	"	1.3725	"	"	"	.3354	-1.71
81	2.6100	2.1130	1cc.	.5cc	.5168	.5150	.36
82	"	2.1100	"	"	"	.5140	.55
84	"	2.1110	"	"	"	.5145	.45
85	"	2.1134	"	"	"	.5152	.30
86	"	2.1900	"	"	"	.5161	.14
87	"	2.0080	"	"	"	.5138	.59
88	"	2.2000	"	"	"	.5164	.09
89	"	2.2090	"	"	"	.5170	.01
91	3.4750	2.4780	1cc.	.6cc	.6046	.6040	.00
92	"	2.5000	"	"	. "	.6100	.89
93	"	2.4900	"	"	"	.6070	.39
94	"	2.4800	"	"	"	.6050	.06
96	"	2.5410	"	"	"	.6200	.25
97	"	2.5220	"	"	"	.6150	.17
98	"	2.4980	"	"	"	.6090	.89

TABLE Vlll.

Results Using FeCl$_3$ as a Carrier.

Test No.	Bromine Used Wt.	%	Bromine Absorbed Wt.	%	Benzene Used	Determined	Error %
99	2.4840	253.8	.3706	41.1	.4392	.0904	79.42
100	"	"	.3105	34.5	. "	.0757	82.75
101	"	"	.2588	28.7	. "	.0631	85.63
102	"	"	.2174	24.1	"	.0530	87.70
103	"	"	.3500	38.8	"	.0715	83.72
104	"	"	.1373	15.2	"	.0335	92.38
105	"	"	.3968	44.1	"	.0968	77.96
106	"	"	.3086	34.2	"	.0729	82.86
107	"	"	.2734	30.3	"	.0667	84.82
108	"	"	.2543	27.2	"	.0620	85.88

TABLE IX.

Effects of Presence of Water.

Test No.	Bromine Used Wt.	Bromine Used %	Bromine Absorbed Wt.	Bromine Absorbed %	Benzene Used	Benzene Determined	Error %
109	2.2289	247.6	.6074	67.5 •	.4392	.1482	66.26
111	"	"	.4936	54.8	"	.1204	72.58
112	"	"	.5281	58.6	"	.1288	70.89
113	"	"	.2566	28.9	"	.0626	85.75
115	"	"	.3457	38.3	"	.0843	80.57
116	"	"	.5423	60.2	"	.1325	69.83

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    670. The percentage of benzol was checked
    by combustion analysis and it was found
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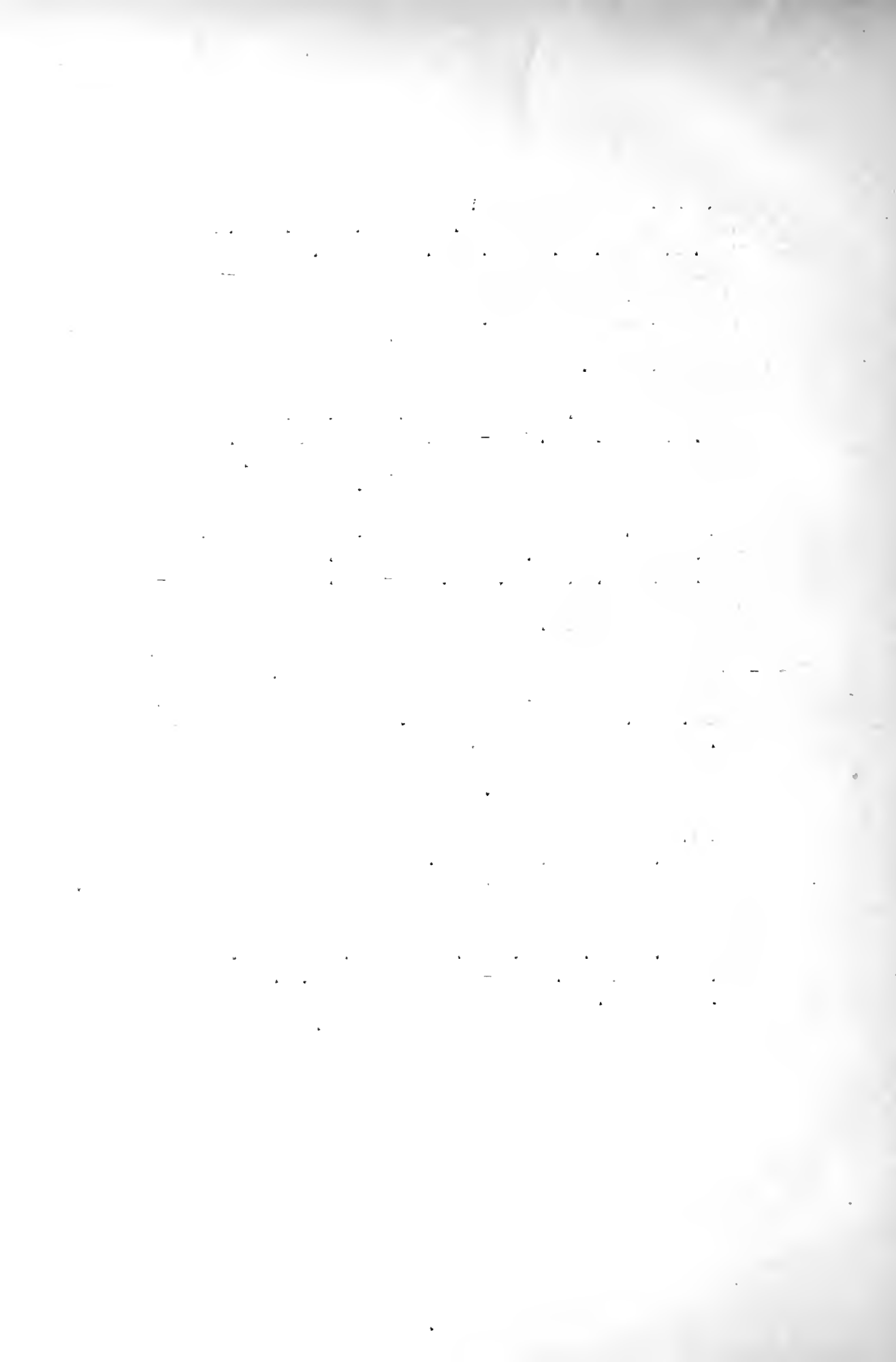
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